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Chalcogenation Reactions of a Stable Ferrocenyldiphosphene: Formation of Thia-, Selena-, and Telluradiphosphiranes

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ABSTRACT: *The reactions of TbtP=PTbt (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) with elemental sulfur and selenium in the presence of triethylamine resulted in the formation of the corresponding thia- and selenadiphosphiranes in 71% and 65%, respectively, whereas the tellurization reaction was unsuccessful probably due to the steric reason. On the other hand, treatment of TbtP=PFc (Fc = ferrocenyl) with elemental sulfur, selenium, and tributylphosphine telluride afforded the corresponding thia-, selena-, and telluradiphosphiranes in 84%, 88%, and 66% yields, respectively. The molecular structures of these three-membered heterocyclic compounds were confirmed by spectroscopic analysis.* Heteroatom Chem 19:443–449, 2008; DOI 10.1002/hc.20449

INTRODUCTION

Since the synthesis and isolation of the first stable diphosphene (Mes*P=PMes*, Mes* = 2,4,6-tri-*tert*-butylphenyl) by taking advantage of kinetic stabilization in 1981 [1], impressive advances have been made in the chemistry of double-bond compounds between heavier group 15 elements (dipnictenes) [2–4]. We have also succeeded in the synthesis of novel doubly bonded systems between heavier group 15 elements, that is, diphosphene (—P=P—), distibene (—Sb=Sb—), dibismuthene (—Bi=Bi—), phosphabismuthene (—P=Bi—), and stibabismuthene (—Sb=Bi—), by taking advantage of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl (Bbt) groups (Fig. 1) [5–17].

There are a several number of reports on the sulfurization and selenization reactions of diphosphenes [8,16,18–22] and the related compounds bearing a low-coordinated phosphorus atom, that is, phosphaalkenes [23–26] and phosphinines [27–29]. It was demonstrated that the sulfurization and selenization reactions of diphosphenes should be convenient for obtaining unique heterocyclic compounds such as thia- and selenadiphosphiranes, since the sulfurization reaction of Mes*P=PMes* using elemental sulfur in the presence of amine was reported to give the corresponding thiadiphosphirane, Mes*P(S)PMes*

Dedicated to Professor Renji Okazaki on the occasion of his 70th birthday.

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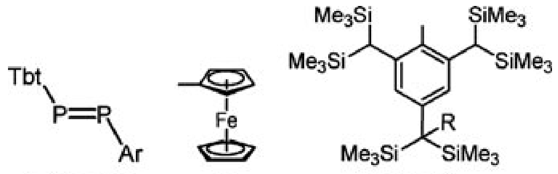


1a (Ar = Fc)
1b (Ar = Tbt)

Fc

Tbt (R = H)
Bbt (R = $SiMe_3$)

FIGURE 1 Diphosphenes **1a** and **1b** (right), ferrocenyl group (center), and bulky substituents, Tbt and Bbt groups (left).

(**2d**), as a stable three-membered heterocyclic compound via the corresponding diphosphene monosulfide, Mes*P=P(=S)Mes* as a metastable intermediate [18,19]. For example, the synthesis of selenadiphosphiranes has been achieved by the treatment of diphosphenes (Mes*P=PMes*, Mes*P=PMes, Mes = 2,4,6-trimethylphenyl [22], and DisP=PDis, Dis=bis(trimethylsilyl)methyl [30]) with elemental selenium. We have also reported the syntheses and characterization of BbtP(Y)PBbt (Y = S (**2c**) and Se (**3c**)) by the chalcogenation reactions of hindered diphosphene, BbtP=PBbt, using elemental sulfur and selenium [8,16]. In contrast to the successful sulfurization and selenization reactions of BbtP=PBbt, it was found that BbtP=PBbt did not undergo tellurization reactions using elemental tellurium or tributylphosphine telluride [8,16]. Although telluradiphosphirane should be a unique and interesting compound from the viewpoint of heteroatom chemistry, no tellurization reaction of a kinetically stabilized diphosphene leading to the formation of the corresponding telluradiphosphirane has been reported so far [31,32].

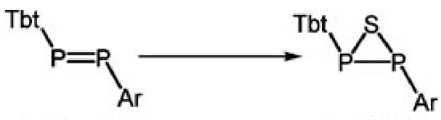
On the other hand, the chemistry of diphosphenes expands to that including functionalized diphosphenes. Particularly, a ferrocenyldiphosphene has attracted much attention as a novel d–π conjugation system. Although Niecke et al. reported the synthesis of Mes*P=PFc, it was unstable and difficult to treat under ambient conditions due to its ready self-dimerization [33]. By contrast, we have reported the synthesis and isolation of TbtP=PFc (**1a**), which was found to be thermally and photochemically stable without any dimerization, and its crystalline structure and redox behavior have been disclosed [10,11]. The first stable ferrocenyldiphosphene can be a useful building block for ferrocenyl-substituted heterocycles, such as chalcogenadiphosphiranes.

In this paper, we report the systematic investigation on chalcogenation reactions of stable ferrocenyldiphosphene **1a** with elemental sulfur, selenium, tellurium, and tributylphosphine telluride. The chalcogenation reactions of TbtP=PTbt (**1b**) have also been performed as a comparative study to elucidate the steric effect of the substituents, Tbt and Fc groups.

RESULTS AND DISCUSSION

Reactions of Diphosphenes **1a** *and* **1b** *with Elemental Sulfur*

In the presence of an excess amount of triethylamine, treatment of **1b** with elemental sulfur in benzene-d_6 in a sealed tube at 100°C for 12 h afforded the corresponding thiadiphosphirane **2b** in 71% isolated yield (Scheme 1). By contrast, it was observed that no reaction of **1b** took place with elemental sulfur in the absence of triethylamine in benzene-d_6 even heating at 100°C in a sealed tube for 48 h. The triethylamine seems to play an important role in the sulfurization reaction, and the role of which can be explained by activation of elemental sulfur in benzene-d_6. The ^{31}P NMR spectrum of **2b** in benzene-d_6 displayed a singlet signal at −72.9 ppm, which is quite similar to those of thiadiphosphiranes **2c** [8] and **2d** [18] (Table 1). Thiadiphosphirane **2b** was very robust in the open air, and no decomposition was observed. On the other hand, the reaction of **1a** with elemental sulfur in benzene-d_6 at room temperature for 30 min resulted in the formation of the corresponding thiadiphosphirane **2a** as yellow crystals in 84% isolated yield (Scheme 1), showing higher reactivity of **1a** toward elemental sulfur than that of **1b**. Although **2a** was stable under an argon atmosphere, gradual decomposition of **2a** was observed in the open air in contrast to the case of **2b**. The ^{31}P NMR spectrum of **2a** showed an AB quartet signal at −98.3 and −86.7 ppm with the phosphorus–phosphorus coupling constant of 203 Hz, which was within the range characteristic of those for the previously reported 2,3-diaryl-1,2,3-thiadiphosphiranes **2c–2f** (Table 1). It should be noted that **1a** was found to undergo sulfurization reaction under milder conditions than that for **1b** probably due to the less hindrance of ferrocenyl group than the

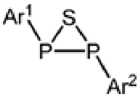


1a (Ar = Fc)
1b (Ar = Tbt)

2a (84%)
2b (71%)

SCHEME 1 Reactions of **1a** and **1b** with elemental sulfur. Reagents and conditions: (1) S_8, benzene, room temperature, 0.5 h (for **1a**) (2) S_8, Et_3 N, benzene-d_6, 100°C, 12 h, in a sealed tube (for **1b**).

TABLE 1 ^{31}P NMR Data of 2,3-Diaryl-1,2,3-thiadiphosphiranes in Benzene-d_6



Compounds	δ_P (ppm)	$^1J_{PP}$ (Hz)	Refs.
Ar^1 = Tbt, Ar^2 = Fc (**2a**)	−86.7, −98.3	203	This work
Ar^1 = Ar^2 = Tbt (**2b**)	−72.9	–	This work
Ar^1 = Ar^2 = Bbt (**2c**)	−71.3	–	8
Ar^1 = Ar^2 = Mes* (**2d**)	−65.1	–	[18]
Ar^1 = Mes*, Ar^2 = Mes (**2e**)	−81.9, −84.0	232.9	[20
Ar^1 = Mes*, Ar^2 = Mox^a (**2f**)	−67.6, −81.8	247.0	[21]

^{a}Mox = 2,4-di-*tert*-butyl-6-methoxyphenyl.

Tbt group. In contrast to the sulfurization reaction of Mes*P=PMes* reported by Yoshifuji et al. [18,19], the corresponding diphosphene monosulfide derivatives, TbtP=P(=S)Tbt and TbtP=P(=S)Fc, were not observed during these reactions as judged by ^{31}P NMR spectroscopy.

Reactions of Diphosphenes **1a** *and* **1b** *with Elemental Selenium*

When a benzene-d_6 solution of **1b** and elemental selenium was heated at 120°C for 12 h in the presence of a large excess amount of triethylamine, the signal for **1b** disappeared and new signals were observed at −57.9 ppm with the satellite signals of 121 Hz in the ^{31}P NMR spectrum (Scheme 2). The observed chemical shifts and coupling constant of the product are similar to those of selenadiphosphiranes **3c–3e** as shown in Table 2, suggesting the formation of the corresponding selenadiphosphirane **3b**. Compound **3b** is thermally stable either up to 250°C in the solid state or up to 120°C in benzene-d_6 in a sealed tube. On the other hand, in the absence of triethylamine, the reaction of **1b** with elemental selenium did not proceed in benzene-d_6 at room temperature as in the case of BbtP=PBbt [8]. Interestingly, treatment of **1a** with 10 molar amount of elemental selenium with a large excess amount of triethylamine in benzene-d_6 at room temperature for 3 h afforded the corresponding selenadiphosphirane **3a** as yellow crystals in 88% isolated yield (Scheme 2). In contrast to **3b**, it was observed that **3a** slowly decomposed in the open air as in the case of **2a**. The ^{31}P NMR spectrum of **3a** showed an AB quartet at −84.1 and −69.7 ppm with $^1J_{PP}$ = 217 Hz, which were similar to those of 2,3-diaryl-1,2,3-selenadiphosphiranes **3c–3e** (Table 2), and these signals have satellite signals of 86.1 and 149 Hz, respectively, due to the neighboring selenium atom. The coupling constants of the observed satellite signals for **3a** suggest the character of hybridization in the phosphorus atoms of **3a**. That is, the former satellite signal (86.1 Hz) should reflect the lower *s*-character of the phosphorus atom than that of the latter signal (149 Hz). Taking into account the ^{31}P NMR data for the reported 2,3-diaryl-1,2,3-selenadiphosphiranes **3b–3e** (Table 2), the signals at −69.7 ppm with $^1J_{SeP}$ = 149 Hz might be assigned to the phosphorus atom bonded to the Tbt group, while the signals at −84.1 ppm with $^1J_{SeP}$ = 86.1 Hz can be attributed to the phosphorus atom bonded to the Fc group. In the ^{77}Se NMR spectrum, **3a** exhibited double of doublet signals with $^1J_{PSe}$ of 86.1 and 149 Hz at −58.3 ppm. These spectral features showed that **3a** possesses the three-membered ring structure with a selenium and two kinds of phosphorus atoms. It can be concluded that the facile formation of **3a** by the selenization reaction of **1a** indicates higher reactivity of the P=P unit of **1a** rather than that of **1b** due to the bulkiness of the substituents.

1a (Ar = Fc)
1b (Ar = Tbt)

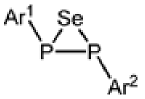
3a (88%)
3b (65%)

SCHEME 2 Reactions of **1a** and **1b** with elemental selenium. Reagents and conditions: (1) Se, Et$_3$ N, benzene-d_6, room temperature, 3 h (for **1a**) (2) Se, Et$_3$ N, benzene-d_6, 120°C, 12 h, in a sealed tube (for **1b**).

Reactions of Diphosphenes **1a** *and* **1b** *with Elemental Tellurium and Tributylphosphine Telluride*

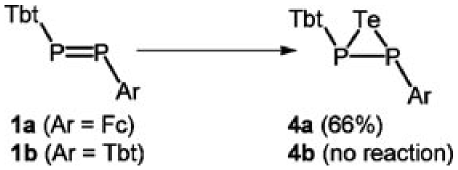
Next, we focused on the reaction of diphosphenes **1a** and **1b** with tellurium sources such as elemental tellurium and tributylphosphine telluride, in the expectation of obtaining the corresponding telluradiphosphirane. Although the syntheses of heterocycles containing phosphorus and tellurium atoms by the reaction of a disilylphosphine with elemental tellurium or that of dichlorophosphine with sodium telluride have been previously published by du Mont and his coworkers [31,32], no report has been published on the formation of the heterocycles by tellurization reactions of a diphosphene using a tellurium source to the best of our knowledge. First, we attempted the reactions of **1a** and **1b** with elemental tellurium as a tellurium source. After heating a benzene-d_6 solution of **1a/1b** with elemental tellurium in the presence of triethylamine at 100/120°C for 24/72 h

TABLE 2 ^{31}P NMR Data of 2,3-Diaryl-1,2,3-selenadiphosphiranes



Compounds	*δ_P (ppm)*	*$^1J_{PP}$ (Hz)*	*Satellite Signal of $^1J_{SeP}$ (Hz)*	*Refs.*
$Ar^1 = Tbt, Ar^2 = Fc$ (**3a**)^a	−69.7, −84.1	217	149, 86.1	This work
$Ar^1 = Ar^2 = Tbt$ (**3b**)^a	−57.9	–	121	This work
$Ar^1 = Ar^2 = Bbt$ (**3c**)^a	−55.3	–	126	[8]
$Ar^1 = Ar^2 = Mes^*$ (**3d**)^b	−47.4	–	131.8	[22]
$Ar^1 = Mes^*, Ar^2 = Mes$ (**3e**)^b	−69.2, −72.0	246.6	–^{c}	[22]

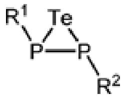
^{a}In C_6D_6.
^{b}In $CDCl_3$.
^{c}The $^1J_{SeP}$ value was not reported.



SCHEME 3 Reactions of **1a** and **1b** with tributylphosphine telluride. Reagents and conditions: (1) n-$Bu_3P = Te$, benzene-d_6, 60°C, 1 h (for **1a**) (2) n-$Bu_3P = Te$, benzene-d_6, 100°C, 12 h, in a sealed tube (for **1b**).

in a sealed tube, no change was observed for **1a/1b** in the ^{31}P NMR spectra, respectively, in contrast to the case of the sulfurization and selenization reactions of **1a** and **1b**. Next, we performed the reactions of **1a** and **1b** with tributylphosphine telluride as a tellurium source, since it is known to work as a better tellurization reagent toward heavier dipnictenes than elemental tellurium [12,16]. Diphosphene **1b** underwent no tellurization reaction with tributylphosphine telluride even at 100°C for 12 h in a sealed tube as in the case of BbtP=PBbt [8,16]. On the other hand, heating a benzene-d_6 solution of **1a** with tributylphosphine telluride (5 eq.) at 60°C for 1 h in a sealed tube gave telluradiphosphirane **4a** as orange crystals in 66% yield after the subsequent purification using gel-permeation chromatography, showing higher reactivity of **1a** toward tributylphosphine telluride than those of **1b** and BbtP=PBbt [8,16] (Scheme 3). The benzene-d_6 solution of **4a** showed an AB quartet signal with $^1J_{PP} = 204$ Hz at −89.6 and −70.6 ppm in the ^{31}P NMR spectrum, which are characteristic values of a three-membered framework for chalcogenadiphosphiranes as summarized in Tables 1–3. The former resonance (−89.6 ppm) had satellite signals of $^1J_{TeP} = 100$ Hz due to ^{125}Te isotope with 7% natural abundance, whereas the latter satellite signals (−70.6 ppm) exhibited $^1J_{TeP}$ of 260 Hz, which is similar to those of three-membered heterocycles containing phosphorus and tellurium atoms, that is, 229 Hz for t-BuP(Te)P(t-Bu) (**4g**) [31,32] and 222 Hz for $Ar_2Si(Te)PMes^*$ ($Ar = 2,4,6$-$Et_3C_6H_2$) [34]. The observed difference of the coupling constants for **4a** can be interpreted in terms of hybridization of the phosphorus atoms. That is, the former satellite signal (100 Hz) should indicate the lower s-character of the phosphorus atom than that of the latter one (260 Hz) as in the case of **3a**. The ^{125}Te NMR spectrum of **4a** in benzene-d_6 showed double of doublet with 100 and 260 Hz at −162 ppm, which appears quite different from that of **4g** ($\delta_{Te} = -696$) [31,32]. Although the reason for the relatively lower field

TABLE 3 NMR Data of 1,2,3-Telluradiphosphiranes



Compounds	*δ_P (ppm)*	*$^1J_{PP}$ (Hz)*	*δ_{Te} (ppm)*	*$^1J_{TeP}$ (Hz)*	*Refs.*
$R^1 = Tbt, R^2 = Fc$ (**4a**)^a	−70.6, −89.6	204	−162	260, 100	This work
$R^1 = R^2 = t$-Bu (**4g**)^b	−70	–	−696	229	[31]

^{a}In C_6D_6.
^{b}In pentane.

chemical shift of **4a** than that of **4g** is unclear at present, it may be explained by the unique properties of the ferrocenyl moiety. The obtained spectral data indicate that **4a** has a three-membered heterocycle composed of a tellurium and two phosphorus atoms. In spite of using dried benzene-d_6 solution in a degassed and sealed tube, telluradiphosphirane **4a** gradually decomposed during the spectroscopic measurement in contrast to the cases of **2a** and **3a**. Anyway, it was found that **4a** can be obtained by the reaction of **1a** with tributylphosphine telluride and reasonably characterized by the spectroscopic data.

CONCLUSION

We demonstrated that the reactions of kinetically stabilized diphosphenes, TbtP=PFc (**1a**) and TbtP=PTbt (**1b**), with elemental sulfur, selenium, and tributylphosphine telluride afforded the corresponding thia- (**2a,b**), selena- (**3a,b**), and telluradiphosphiranes (**4a**), respectively. The molecular structures of three-membered heterocycles **2a–4a** were characterized by NMR spectroscopy. These heterocycles can be handled as stable compounds in the open air except the ferrocenyl derivatives, **2a, 3a**, and **4a**. Although stable diphosphene **1a** was prevented from the dimerization reaction by the steric protection afforded by the combination of Tbt and Fc groups, it was revealed that reactions of **1a** with elemental sulfur and selenium proceed under milder conditions as compared with those for **1b** bearing two Tbt groups. Moreover, it was observed that the reaction of **1a** with tributylphosphine telluride afforded the corresponding telluradiphosphirane, a three-membered heterocyclic compound composed of a tellurium and two phosphorus atoms, as an isolable compound without any oligomerization, whereas diphosphene **1b** did not undergo a tellurization reaction using elemental tellurium or tributylphosphine telluride as a tellurium source. The exclusive formation of telluradiphosphirane **4a** by the reaction of **1a** with tributylphosphine telluride was the first example for the tellurization reaction of a diphosphene, and the key to the successful formation of **4a** should be the adaptation of the appropriate size of steric protection groups.

EXPERIMENTAL

General Procedures

All reactions were carried out under an argon atmosphere or in a degassed and sealed tube, unless otherwise noted. All solvents were purified by standard methods and then dried by using an ultimate solvent system (Glass Contour Company) [35]. Benzene-d_6 for the NMR spectroscopy was dried by using a potassium mirror prior to use. Preparative thin-layer chromatography (PTLC) and column chromatography were performed with Merck Kieselgel 60 PF254. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or 918 equipped with JAI-gel 1H and 2H columns (Japan Analytical Industry Co., Ltd., Tokyo, Japan) with toluene as an eluent. ^{1}H NMR (400 or 300 MHz) and ^{13} C NMR (100 or 75 Hz) spectra were measured in C_6D_6 with a JEOL AL-400 or 300 spectrometer using C_6HD_5 ($\delta = 7.15$ ppm) for ^{1}H NMR spectra, and C_6D_6 ($\delta = 128.0$ ppm) for ^{13}C NMR spectra as internal standards, respectively. ^{31}P (120 MHz), ^{77}Se (57 MHz), and ^{125}Te NMR (94 MHz) spectra were measured in C_6D_6 with a JEOL AL-300 spectrometer using 85% H_3PO_4 ($\delta = 0$ ppm), Ph_2Se_2 ($\delta = 460$ ppm), and Ph_2Te_2 ($\delta = 450$ ppm) as external standards, respectively. High-resolution mass spectral data were obtained on a JEOL SX-270 mass spectrometer. All melting points were determined on a Yanaco micromelting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Elemental sulfur was purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and purified by recrystallization from benzene before use. Elemental selenium was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Triethylamine was purchased from Nacalai Tesque, Inc. and purified by distillation before use. Celite® (diatomacenous earth) was purchased from Kanto Chemical Co., Inc. and dried at 200°C for 24 h before use. TbtP=PFc (**1a**) [10] and TbtP=PTbt (**1b**) [8] were prepared according to the procedures reported in the literature. Chemical data for TbtP(S)PTbt (**2b**) and TbtP(Se)PTbt (**3b**) were shown in the literature [17].

*Reaction of TbtP=PFc (**1a**) with Elemental Sulfur*

To a solution of TbtP=PFc (**1a**) (39.2 mg, 49.0 μmol) in benzene (10 mL, an elemental sulfur (S_8, 15.7 mg, 490 μmol as a sulfur atom) at room temperature was added. After the reaction mixture was stirred at room temperature for 30 min, the solution was filtered to remove unreacted elemental sulfur, and the filtrate was concentrated. The residue was purified by GPLC to afford thiadiphosphirane **2a** (34.3 mg, 41.3 μmol, 84%) as yellow crystals. **2a**: mp 155°C (dec); ^{1}H NMR (300 MHz, C_6D_6, 25°C) δ 0.14 (s, 18H, $Si(CH_3)_3$), 0.27 (s, 18H, $Si(CH_3)_3$), 0.34 (s, 18H, $Si(CH_3)_3$), 1.43 (s, 1H, CH), 3.11 (s, 1H, CH), 2.25 (s, 1H, CH), 3.95 (br, 1H, C_5H_4), 4.03 (br, 1H, C_5H_4), 4.04 (s, 5H, C_5H_5), 4.17 (br, 1H, C_5H_4), 4.60 (br, 1H, C_5H_4), 6.48 (br s, 1H, $C_6 H_2$), 6.61 (br s, 1H, $C_6 H_2$); ^{13}C NMR (75 MHz, C_6D_6, 25°C) δ 0.62 (s, CH_3), 0.92 (s, $CH_3 \times 2$), 30.07 (br, CH × 2), 30.94 (s, CH), 69.69 (d, $J_{PC} = 4.3$ Hz, C_5H_4), 71.22 (s, C_5H_5), 71.94 (d, $J_{PC} = 5.5$ Hz, C_5H_4), 73.69 (s, C_5H_4), 74.44 (s, C_5H_4), 75.97 (dd, $J_{PC} = 61.9$, 11.4 Hz, C_5H_4), 122.68 (br, *m*-C_6H_2), 127.75 (br, *m*-C_6H_2), 137.81 (br, *o*-C_6H_2), 143.17 (br, *o*-C_6H_2), 144.34 (s, *p*-C_6H_2), 149.06 (m, *ipso*-C_6H_2); ^{31}P NMR (120 MHz, C_6D_6, 25°C) δ −98.3, −86.7 (ABq, $^1J_{PP} = 203$ Hz); HRMS (FAB) found: *m/z* 830.2493 ($[M]^+$), Calcd for $C_{37}H_{68}FeP_2SSi_6$: 830.2482.

*Reaction of TbtP=PTbt (**1b**) with Elemental Sulfur*

A suspension of TbtP=PTbt (**1b**) (70.0 mg, 60.0 μmol), elemental sulfur (S_8, 19.2 mg, 600 μmol as a sulfur atom), and triethylamine (90 μL, 0.65 mmol) in benzene-d_6 (0.7 mL) was placed in an NMR tube. After three freeze–pump–thaw cycles, the tube was sealed. When the tube was heated at 100°C for 12 h, the signal for **1b** disappeared and that for **2b** appeared in the ^{31}P NMR spectrum. The tube was opened and evaporated, and hexane was added to the residue. After the solution was filtered through Celite®, purification by using PTLC (hexane) afforded thiadiphosphirane **2b** (51.1 mg, 42.6 μmol, 71%) as pale yellow crystals.

*Reaction of TbtP=PFc (**1a**) with Elemental Selenium*

A benzene-d_6 suspension (0.7 mL) of TbtP=PFc (**1a**) (28.4 mg, 35.6 μmol), elemental selenium (28.1 mg, 356 μmol), and triethylamine (87 μL, 0.63 mmol) were degassed and sealed in an NMR tube. After standing at room temperature for 3 h, the ^{31}P NMR signals for **1a** completely disappeared. The suspension was filtered to remove unreacted selenium powder and purified by GPLC to afford selenadiphosphirane **3a** (27.5 mg, 31.3 μmol, 88%) as orange crystals. **3a**: mp 138°C (dec); ^{1}H NMR (400 MHz, C_6D_6, 25°C) δ 0.13 (s, 18H, $Si(CH_3)_3$), 0.14 (s, 18H, $Si(CH_3)_3$), 0.26 (s, 18H, $Si(CH_3)_3$), 1.42 (s, 1H, CH), 3.24 (br s, 1H, CH), 3.38 (br s, 1H, CH), 3.96 (s, 1H, C_5H_4), 4.04 (s, 5H, C_5H_5), 4.05 (s, 1H, C_5H_4), 4.18 (s, 1H, C_5H_4), 4.63 (s, 1H, C_5H_4), 6.48 (br s, 1H, C_6H_2), 6.62 (br s, 1H, C_6H_2); ^{13}C NMR (100 MHz, C_6D_6, 25°C) δ 0.62 (s, CH_3), 0.91 (s, CH_3), 0.94 (s, CH_3), 29.67 (s, CH), 30.06 (s, CH), 30.95 (s, CH), 71.07 (d, $J_{PC} = 5.0$ Hz, C_5H_4), 71.09 (s, C_5H_5), 72.10 (d, $J_{PC} = 5.0$ Hz, C_5H_4), 74.57 (s, C_5H_4), 74.89 (dd, $J_{PC} = 63.1$, 14.0 Hz, *ipso*-C_5H_4), 75.21 (s, C_5H_4), 122.88 (br, *m*-C_6H_2), 127.79 (br, *m*-C_6H_2), 141.50 (br, *o*-C_6H_2), 144.30 (br, *o*-C_6H_2), 144.46 (s, *p*-C_6H_2), 149.36 (br, *ipso*-C_6H_2); ^{31}P NMR (120 MHz, C_6D_6, 25°C) δ −84.1 (d, $^1J_{PP} = 217$ Hz with the satellite signal of $^1J_{SeP} = 86.1$ Hz), −69.7 (d, $^1J_{PP} = 217$ Hz with the satellite signal of $^1J_{SeP} = 149$ Hz); ^{77}Se NMR (57 MHz, C_6D_6, 25°C) δ −58.3 (dd, $^1J_{PSe} = 149$, 86.1 Hz); HRMS (FAB) found: *m/z* 878.1920 ($[M]^+$), Calcd for $C_{37}H_{68}FeP_2{}^{80}SeSi_6$: 878.1926.

*Reaction of TbtP=PTbt (**1b**) with Elemental Selenium*

A suspension of TbtP=PTbt (**1b**) (70.0 mg, 60.0 μmol), elemental selenium (47.4 mg, 600 μmol), and triethylamine (90 μL, 0.65 mmol) in benzene-d_6 (0.8 mL) was placed in an NMR tube. After three freeze–pump–thaw cycles, the NMR tube was sealed. After heating the tube at 120°C for 12 h, the signals for **1b** disappeared in the ^{31}P NMR spectrum. The tube was opened and evaporated, and hexane was added to the residue. After the resulting solution was filtered through Celite®, purification by using PTLC with hexane as an eluent afforded selenadiphosphirane **3b** (48.7 mg, 39.1 μmol, 65%) as pale yellow crystals.

*Reaction of TbtP=PFc (**1a**) with Tributylphosphine Telluride*

Diphosphene **1a** (62.5 mg, 78.2 μmol), tributylphosphine telluride (168 mg, 391 μmol), and benzene-d_6 (0.7 mL) were placed in an NMR tube. After three freeze–pump–thaw cycles, the NMR tube was evacuated and sealed. The solution was heated at 60°C for 1 h, during which time the original purple color changed to orange and the signals for **1a** disappeared in the ^{31}P NMR spectrum. The tube was opened, and the insoluble materials were removed by filtration through Celite®. After removal of the solvent, the reaction mixture was separated by GPLC to afford TbtP(Te)PFc (**4a**) (47.8 mg, 51.6 μmol; 66%). **4a**: mp 143°C (dec); ^{1}H NMR (300 MHz, C_6D_6, 25°C) δ 0.11 (s, 18H, $Si(CH_3)_3$), 0.27 (s, 18H, $Si(CH_3)_3$), 0.32 (s, 18H, $Si(CH_3)_3$), 1.43 (s, 1H, CH), 3.49 (br s, 1H, CH), 3.59 (br s, 1H, CH), 3.96 (m, 1H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.12 (m, 1H, C_5H_4), 4.16 (m, 1H, C_5H_4), 4.67 (m, 1H, C_5H_4), 6.51 (br s, 1H, C_6H_2), 6.64 (br s, 1H, C_6H_2); ^{31}P NMR (120 MHz, C_6D_6, 25°C) δ −89.6 (d, $^1J_{PP} = 204$ Hz, $^1J_{TeP} = 100$ Hz), −70.6 (d, $^1J_{PP} = 204$ Hz, $^1J_{TeP} = 260$ Hz); ^{125}Te NMR (94 MHz, C_6D_6, 24°C) δ −162 (dd, $^1J_{PTe} = 260$, 100 Hz); HRMS (FAB) found: *m/z* 928.1852 ($[M + H]^+$), Calcd for $C_{37}H_{69}FeP_2Si_6{}^{130}Te$: 928.1821.

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